NOTES ON

LUMINOUS AND NON-LUMINOUS COMBUSTION.

By B. H. THWAITE, C.E.

NEARLY half a century has elapsed since the most illustrious of our past great scientific experimental investigators—Michael Faraday—used to delight his audience at the Royal Institution, not only by the simplicity and originality of his experimental demonstrations, but also by the lucidity of his verbal description of the phenomena associated with chemical and electrical energy. The theory that Faraday enunciated in his lectures to explain the cause of luminosity of combustion was that introduced by his brilliant predecessor, Sir Humphry Davy. This theory was accepted by the author, in the absence of direct experiment proving it to be wrong. It has now been challenged by Professor Harold B. Dixon, F.R.S.[*] It is only by critical analysis that one finds out the truth ; and therefore we are indebted to Professor Dixon for raising an interesting inquiry.

Modern chemists and physicists have generally accepted the Davy-Faradaic theory. Amongst them may be mentioned : Soret, the first to optically establish, by experimental proof, the fact that the luminous portion of an ordinary batswing or Argand flame is solid; Mees, who developed Soret's method of proof; also Hirn, Knapp, Heumann, and Wulner ; Berthelot, whose experimental researches into the domain of thermo-physics are beyond praise—and whose magnificent work, " Essais de Mécanique Chimique "—is a monument of enduring fame, to the honour and glory of French science; and Mendeléef.

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[*] See *Journal of Gas Lighting*, Vol. LXV., p. 214.

All these accept, more or less in its entirety, what we will call, for brevity and distinction, the Davy-Faradaic theory. Subject to certain qualifications, the author still believes, and hopes to be able to prove, this theory to be sound, and far more nearly allied to the exact truth, than the one now held by Professor Dixon, based as that gentleman's theory is, upon experience of combustion phenomenon that has little in common with the open or unrestrained, or free and sequential character of combustion at atmospheric pressures.

The author's first article, in which certain conclusions are challenged, was intended to show that the luminous combustion of gas burnt *à la* Welsbach, or in such a way that the heat of combustion of the hydrogen and the carbon is transmitted to a refractory and inoxidizable medium, is very greatly superior to the luminous efficiency of the combustion of gas burnt (say) in an ordinary batswing burner, in which the luminosity is based on the incandescence of the carbon resulting from the combustion of the hydrogen. Described with more detail, both these methods of combustion involve, as necessary qualifications—

(1) That the combustion of the hydrocarbonaceous gas shall be gradual.

(2) That the gas shall flow during combustion from an orifice at a certain pressure.

(3) That this pressure shall be a little above that of the atmosphere.

(4) That the combustion itself shall be effected at the pressure of the atmosphere.

The conditions of combustion now under comparison do not include one that would be subordinate to any of the following qualifications :—

(A) The preadmixture of the hydrocarbonaceous gas and air in explosive proportions.

(B) The enclosure of such gases in a closed vessel before and after combustion.

(C) Neither does it permit the inclusion of a condition that permits the combustion of the hydrocarbonaceous combustible, *ab initio* in a solid form, as distinct from a combustible of a gaseous character.

It is thought necessary to make these specific and fundamental distinctions, because the characteristic of the combustion and the conditions that would apply to one form of combustible and

method of its oxidation, do not altogether, if at all, apply to those of another. To raise objections (based on a knowledge of one, and a distinctive, method of combustion, and involving certain conditions) to theories that are only intended to apply to quite distinctive methods of combustion, is obviously untenable. As evidence of the importance of this distinction, it is quite clear that a combustion effected according to the formula given by Professor Dixon for the combustion of acetylene and ethylene, and producing carbon monoxide, could not produce a very luminously explosive combustion ; and such an equation has little resemblance to one representing the action of the methods of combustion which are the subject of this and former memoirs presented by the author.

Divested of irrelevant comparisons, Professor Dixon's article merely contains references to certain laboratory experiments of Professor Smithells, to substantiate the *rationale* of his other objections. Here, again, we have a distinctive form of combustion—this time *à la* Argand. The meaning of the results in Professor Smithells's investigations is not at all conclusive. Even Professor Dixon, to use his own words, admits "it is conceivable that the hydrogen burns first." So that he may be said to have failed, in his article, to advance any experimental proof to upset the Davy-Faradaic theory.

As both Berthelot's results, and the others referred to, bear more directly upon the subject under discussion, if we are to be guided by experiment, and not by imagination, we are bound to admit that the Davy-Faradaic theory, explaining the phenomenon of a hydrocarbon gas-flame burning at the pressure of the atmosphere, is true to nature, and is not a fallacy, except so far as it includes, by Davy's stated qualification to his original theory the suggestion that the oxidation of the solid carbon following on that of the hydrogen adds by its heat to the luminous intensity to any appreciable degree.

Influence of Thermolysis.

The author's experience in the use of hydrocarbonaceous fuels—solid, liquid, and gaseous—has satisfied him that the stability of nearly all the hydrocarbons is destroyed when brought under the influence of temperatures above 2000 Fahr. This thermic influence induces hydrocarbon decomposition, which we will call "thermolysis," or the splitting up by heat of hydrocarbon compounds. This thermolytic action is a part of the explanation of the sequence of action of ordinary carbon luminous combustion.

The oxidation of the free hydrogen as well as of part of the hydrogen of the decomposed hydrocarbons, establishes a zone of high temperature. In this zone the hydrocarbon structure, still undecomposed, collapses; and both the hydrogen and the carbon are set free. The hydrogen is oxidized to water vapour; and the carbon, if there is oxygen present, is oxidized to carbon monoxide, or, if oxygen is not present in equivalent proportions, is set free as a solid and in a highly incandescent condition—providing the luminous proportion of the flame.

The influence of this thermolytic action is well known. The author has shown elsewhere that, owing to this influence, the principle of preheating gaseous fuel, employed in the Siemens form of furnace, is bad, because the exposure of the hydrocarbon gas to the influence of highly-heated bricks tends to throw down the carbon part of the hydrocarbon into the recuperator chamber, and a great part of the thermic assets of the fuel is thus lost. The same action of thermolysis occurs in the production of enriched water gas. If the fixing chambers are too hot, the hydrocarbons are thermolytically decomposed, and the lighting value of the gas is seriously impoverished.

The formula of complete thermolysis, applied to one of the simple hydrocarbons, may be thus expressed :

$$C_2H_6 + \text{thermolytic influence} = 2\,C + 6\,H\,;$$
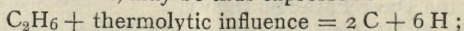
the former being deposited in a solid, while the latter is in a gaseous condition.

Marsh Gas (CH_4) + thermolytic influence = $CH_4 = C + 4\,H.$
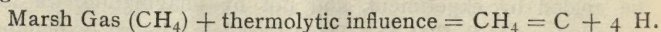
Acetylene exposed to only a relatively high temperature is decomposed into marsh gas and free carbon thus :

$$C_2H_4 + \text{thermolytic influence} = CH_4 + C.$$
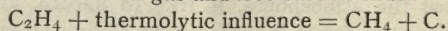
The heat-absorption involved in the act of thermolytically separating a given weight of hydrocarbon is the same whether the two elements, hydrogen and carbon, are oxidized simultaneously or in sequence. The object of the author's preceding article was intended to show a comparison of efficiency between two methods of combustion; and he decided to neglect those factors on each side of the comparative equations, which were the same for both systems of combustion, especially in the face of the uncertainty of the correcting factors.

It is well known that the difference between the heat of combustion for marsh gas (C_2H_4) first calculated separately, and secondly as actually obtained in the calorimeter, is $21\cdot75 : 24\cdot75$; whereas olefiant gas, whether calculated separately or burnt in a calorimeter, is the same—proving there is a physical difference between the form of carbon in the one and in the other.

The author notices that Professor Dixon semi-apologetically refers to the purposely omitted correction for the absorption of heat in the thermolysis of the hydrocarbon, and its influence on the total heat produced when compared with the burning of the two elements separately.

The Influence of the Heat from the Oxidation of the Carbon on its Non-Luminous Intensity.

The argument advanced by both Professor Dixon and Mr. Young—that part of the heat of the combustion of the carbon burnt to carbon dioxide should be credited as assisting to build up the degree of incandescence of the carbon part of the flame—is not reasonable. A stream of atoms of incandescent carbon meet equivalent atoms of oxygen; the result being the annihilation of the solid character forming the basis of incandescence, and its displacement by a gaseous and non-luminous product. Any heat of a sensible kind associated with the gaseous products of combustion ascends above the zone of action as rapidly as the cold air rises to supply the carbon with its equivalent oxygen.

Here is an argument proving the fallacy of Professor Dixon's suggested correction : Immediately a light is applied to lighting gas, it illuminates instantly with its full and mature measure of light. Did it not do so, then Professor Dixon might, with some support, suggest that part of the heat resulting from the oxidation of the carbon is, in some inexplicable way, transferred to atoms of carbons following the *disappearance* of those atoms immediately preceding, and which have disappeared as a result of their oxidation to carbon dioxide—a colourless gas.
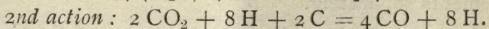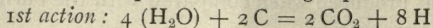
In the combustion of a carbonaceous solid, we have an aggregation of atoms attached to each other, not like the atoms of carbon that are separated from the hydrogen zone of oxidation of a gas-flame. When carbon atoms are aggregated together, the heat resulting from the oxidation of one atom is communicated to its immediate associates, until it is transferred more or less to the entire mass. It will perhaps be conceded that the carbon incandescence of (luminous) gas combustion is not, in any appreciable degree, due to the oxidation of the carbon, in the absence of positive data to the contrary.

Luminous Hydrocarbon Flame Combustion involves the Reactions common to Water-Gas Production.

The argument raised by Professor Dixon that, if the Davy-Faradaic theory is correct, it would involve the production of water gas, is accepted as true to a certain extent ; and if Professor Dixon will accept the results to be given farther on as

proving the existence of the action of water-gas production, he will then be compelled to acknowledge that the Davy-Faradaic theory is correct.

We will define the equation of water-gas production thus:

$1st\ action:$ $4\ (H_2O) + 2\ C = 2\ CO_2 + 8\ H$

$2nd\ action:$ $2\ CO_2 + 8\ H + 2\ C = 4\ CO + 8\ H.$

In the combustion of a hydrocarbonaceous gas, the action of combustion may be thus sequentially described:

(A) Free hydrogen oxidized.

(B) Part of proportion of higher hydrocarbons thermolytically decomposed.

(C) The water vapour resulting from the oxidation of the free hydrogen (A) in contact with the incandescent carbon (B) results in the formation of carbon monoxide and the freeing of the hydrogen.

(D) The complete decomposition of the remainder of the hydrocarbons; the hydrogen burning, and the carbon being set free in an atomized and incandescent condition.

(E) The incandescent carbon is either brought into contact with air or with the water resulting from the oxidation of the hydrogen; producing in the former instance carbon dioxide, and in the latter the carbon monoxide compound. If there is an excess of air, the latter gas is oxidized to carbon dioxide.

Granting that this stated sequence of action is true to nature (and M. Landolt's results leave little doubt on this point), we have the superior value of combustion, effected à la Bunsen, absolutely confirmed.

It may be argued that the partial oxidation of the carbon of the hydrocarbons to carbon monoxide would provide a certain proportion of heat in the non-luminous zone; but the maximum temperature that could result from this merely partial carbon oxidation would not raise to incandescence (of any luminous value) any atoms of unoxidized carbon passing through the zone of such carbon monoxidation. Every atom of carbon so oxidized takes away from the carbon density of the flame.

The author, assisted by Mr. Horace Allen, has made some experiments to discover the ratio of carbon deposition to the total carbon in ordinary naked flame combustion. From these experiments, he deduced the fact that only a certain and varying proportion of the carbon was utilized in any hydrocarbon batswing or similar flame in incandescence light giving. It may be stated that not more than 30 per cent. of the original carbon

assets of a hydrocarbonaceous flame are deposited in the luminous area of the flame ; the remaining part of the carbon— burning to carbon monoxide, and afterwards to carbon dioxide— clearly provides no illuminating value, because the carbon in a solid form, to which the heat might be given, disappears on the oxidation to either carbon monoxide or carbon dioxide, both gases having no luminous value. Whereas the complete oxida- tion of the carbon to carbon dioxide in combustion effected *à la* Welsbach or equivalent system, and the inoxidizable network to which such heat is transmitted, permits the full utilization of the heat; and as the carbon is instantly oxidized to carbon dioxide, the water gas reactions occurring in ordinary flame combustion cannot take place.

The Restricted Efficiency of Recuperative Combustion.

The fact of the partial oxidation of the carbon of the hydro- carbons adds to the value of the recuperative principle, because, although the carbon, oxidized to carbon monoxide and then to carbon dioxide, gives no luminosity in itself, the heat resulting from its oxidation is partially transmitted in a sensible form to the air flowing to support combustion. The heat thus supplied is added to that produced by the oxidation of the hydrogen, and a higher degree of luminosity is the consequence. Unfortu- nately, no form of recuperator can give a perfect return of the heat introduced into it—a great portion being lost through the chimney; and this is why the recuperator lamp is inferior in light-giving efficiency to the incandescence lamp of the Welsbach type.

Landolt's Results Tabularly Expressed.

Height in Millimetres at which the Gas Tested was Aspirated above Emission-Point in Ordinary Burner, of 0·007 mm. Diameter.		Volumetric Proportions shown graphically by figs. 1 & 2 (pp. 8, 9).							
		H.	CO.	CO$_2$.	N.	O.	C$_4$H$_8$.	C$_2$H$_4$.	CH$_4$.	H$_2$O.
		%	%	%	%	%	%	%	%	%
A	50	2·59	5·45	7·01	66·59	..	0·58	0·60	0·79	16·39
	40	3·43	5·26	5·62	64·01	..	0·77	0·90	2·82	17·19
	30	4·99	4·68	4·81	59·18	..	1·00	1·55	6·92	16·87
	20	2·23	5·71	4·11	57·25	0·19	1·34	1·86	11·52	15·79
B	10	12·45	9·71	1·95	32·20	0·65	2·65	3·59	25·14	9·66
	0	20·34	6·59	1·74	26·40	0·59	2·75	3·80	30·31	7·48

A.—Luminous.   B.—Non-luminous.

Remarks.—The analytical tests made by the author and Mr. Allen confirm the fact here shown, that practically *no carbon dioxide* is produced in a height of 15 millimetres of the non-luminous zone. *Vide Addendum* (p. 10).
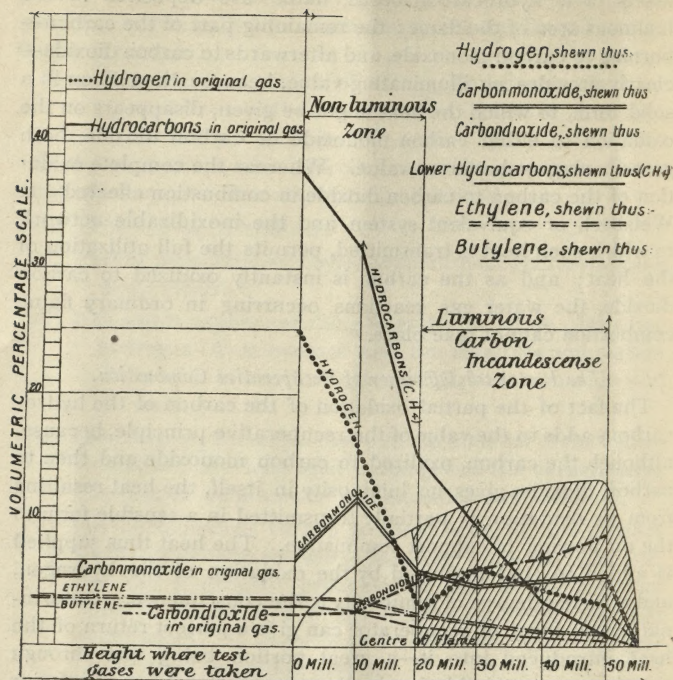
FIG. I.—PREPARED BY B. H. THWAITE FROM THE RESULTS OF
LANDOLT'S INVESTIGATIONS.

Landolt's results, given tabularly and presented graphically,
appear to show that, in the combustion of a hydrocarbona-
ceous gas, in an ordinary batswing burner—

(1) The hydrogen is oxidized before the carbon.

(2) The combustion of the hydrogen produces the heat by
which the hydrocarbons are thermolytically decom-
posed.

(3) The thermolytic action proceeds progressively.

(4) Part of the carbon of the decomposed hydrocarbon is par-
tially oxidized to carbon monoxide, but not to carbon
dioxide.

(5) The hydrogen is oxidized to water, and is partly reduced
to hydrogen by the carbon, but is eventually re-oxidized
to water.

(6) Only a portion of the carbon is liberated in a free and
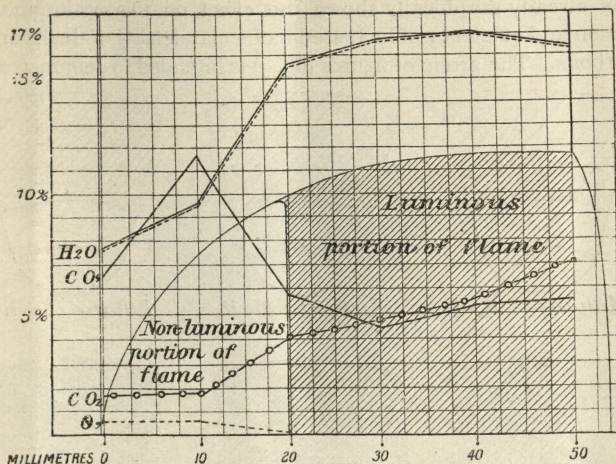incandescent condition, to form the luminous portion of
a flame.

17 %
:5 %
10 %
H2O
C O
5 %
Luminous portion of flame
Non-luminous portion of flame
C O
θ
MILLIMETRES 0   10   20   30   40   50

FIG. 2.—GRAPHIC DIAGRAM PREPARED BY B. H. THWAITE FROM
THE RESULTS OF LANDOLT'S INVESTIGATIONS.

Influence of Flame Juxtaposition.

The explanation of the fact that two luminous carbon flames
placed in juxtaposition give a rather higher photometric
efficiency than a single flame, is probably as follows : The flow
of atoms, in rapid vertical movement, makes the flame surface
more dense. The interspace between one atom and another in
one flame may, in another closely adjoining and parallel flame,
have a corresponding atom-filled space ; and the luminous
radiation may be considered to be equivalent in intensity to an
area of luminosity of twice the density of the single flame. The
same principle partly applies to the Argand method of com-
bustion. There is this objection, that part of the luminous rays
from the two parallel and inner faces may be absorbed by the
atoms of carbon. But this degree of radiant and luminous loss
must be small, because the flow of the carbon in atomized form
may be taken to be equal to the velocity of the gas emitted from
the burner orifice ; and this velocity compared with that of light
is as 1 : 3,000,000.

The more dense a given hydrocarbon, the more concentrated
is its luminous emitting surface. If our optic nerves were suffi-
ciently sensitive, we should be able to discern the intervals
between the atoms of carbon as they emerge from the zone of
hydro-oxidation. We, however, realize the increased luminosity
due to the increase in the number of carbon atoms by the
superior luminosity of the higher hydrocarbons. The author

has already graphically shown the effect on thermo-luminous action and efficiency of increased molecular density of the hydro-carbons. The group of figures (fig. 3) is intended to demonstrate

Methane (C H 4)   Acetylene (C2 H2)   Ethane (C2 H6)

Propane (C3 H8)   Butylene (C4 H8)   Pentane (C5 H12)
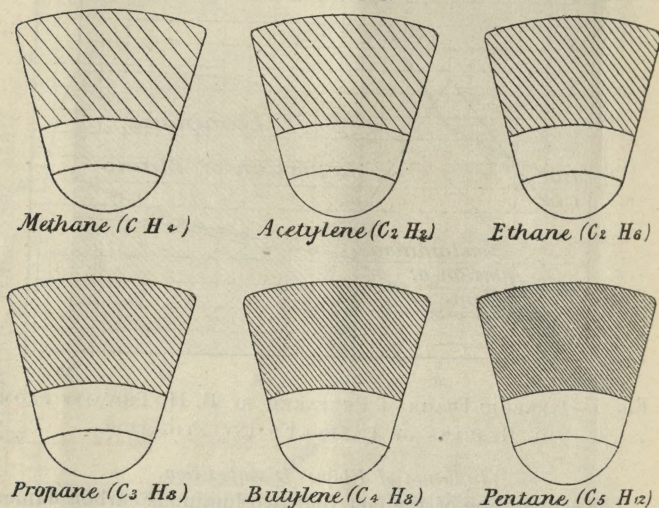
FIG. 3.—DIAGRAMS SHOWING GRAPHICALLY THE DENSITIES OF SOME HYDROCARBONS.

graphically the greater intensity of surface luminosity of different hydrocarbons, and is an attempt to show the exact influence of increased molecular density by shaded surfaces. The density and corresponding luminous efficiency is the measure of the deepness of the hatched surface, which represents the luminous portion of the flame.

ADDENDUM.

The author, in conjunction with Mr. Horace Allen, made a few determinations to ascertain whether the carbon in the London retort gas, either in association with hydrogen as hydrocarbon or with oxygen as carbon monoxide, was oxidized, in the non-luminous part of the flame, to carbon dioxide. In the test, when employing the ordinary jet or batswing flame character of flame combustion, a No. 8 Sugg's burner was employed. The gas was burnt at the ordinary pressure employed by The Gaslight and Coke Company; and the gas was taken from the identical main from which the gas was obtained for the gas-engine tests that were referred to in the last article contributed by the author.* In aspiring the gas (products of

* See *Journal of Gas Lighting*, Vol. LVIII., p. 205.

combustion), great care was exercised that it should be truly representative, and that only the products of combustion would be included.

In the first two tests, identified as determinations A and B, the flame was of the shape shown in fig. 4. In the A
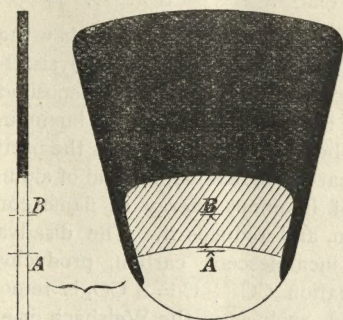

Gas taken from centre
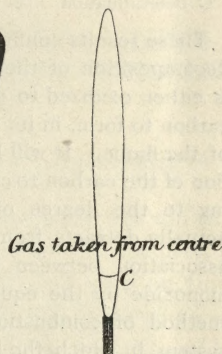
FIG. 4.—GASES DRAWN OFF AT   FIG. 5.
POINTS A, B, AND C.

determinations, the gas was aspired from the flame at the level marked by the letter A in fig. 4, or at a height of $\frac{3}{4}$ inch above the burner tip in the non-luminous zone. In the B determination, the gas was drawn at a height of 1 inch above the burner tip, and at the point marked B, just within the zone of non-luminous combustion, and on the margin of the luminous portion of combustion.

Percentage of Volumetric Carbon Dioxide.	Actual Percentage of Total Carbon Oxidized to Carbon Dioxide, less Original Proportion contained in the Gas (0·5 per Cent.)	Percentage Proportion remaining to be Oxidized in Luminous Part of Flame.
A Determination, 0·8 per cent.		
Proportion due to combustion equals (0·8−0·5) 0·3 per cent.	3·6 per cent. ..	96·4 per cent.
B Determination, 2·0 per cent		
Proportion due to combustion equals (2·0−0·5) 1·5 per cent.	23·8 ,, ..	76·2 ,,

The proportion of carbon dioxide that should be found if all the carbon were oxidized to CO_2 with the atmospheric equivalent, is taken as being equal to 8·3 per cent.

In the C determination, the batswing (No. 8) burner was removed, and the gas was allowed to flow quite freely from a pipe of $\frac{1}{8}$ inch bore, when the combustion assumed the form shown in fig. 5. The products of combustion were drawn from

the flame at the point C, or at a height of $1\frac{7}{8}$ inches above the burner.

Percentage of Volumetric Carbon Dioxide.	Actual Percentage of Total Carbon Oxidized to Carbon Dioxide, less Original Proportion contained in the Gas (0·5 per Cent.).	Percentage Proportion remaining to be Oxidized in Luminous Part of Flame.
C Determination, 2 per cent.	23·8 per cent.	76·2 per cent.

These results confirm those of Landolt, and show that, on the decomposition of the hydrocarbons by thermolysis, the carbon is either oxidized to carbon monoxide, or is deposited as solid carbon to form, in its incandescent state, the luminous portion of the flame. It will be fully recognized that the partial oxidation of the carbon to carbon monoxide, instead of aiding or adding to the degree of luminous energy of flame combustion, actually detracts from, and reduces it. The disadvantage of association between incandescent carbon, producing carbon monoxide by the equation $CO_2 + C = 2\ CO$, is removed in a method of combustion such as is the Welsbach or equivalent system, in which the luminous part can neither (under the conditions established) oxidize nor dioxidize. Hence the value of the Welsbach or other similar system, in which the incandescent agent neither reduces the carbon dioxide, nor becomes converted into gas by its own oxidation.